# Synthesis and Characterization of Porous Metal Oxides in Imidazolium Ionic Liquids

**A Dissertation**
**Submitted in partial fulfillment**

**FOR THE DEGREE**
**OF**
*MASTER OF SCIENCE IN CHEMISTRY*

*UNDER THE ACADEMIC AUTONOMY*
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

**By**
*Chinmayee Priyadarshini*

Under the Guidance of
**Dr. Priyabrat Dash**

**DEPARTMENT OF CHEMISTRY**
**NATIONAL INSTITUTE OF TECHNOLOGY**
**ROURKELA – 769008**
**ODISHA**

# CERTIFICATE

**Dr. Priyabrat Dash**
*Assistant Professor*
**Department of Chemistry**
**NIT, Rourkela-ODISHA**

*This is to certify that the dissertation entitled* ***"Synthesis and Characterization of Porous Metal oxides in Imidazolium Ionic Liquids"*** *being submitted by* ***Chinmayee Priyadarshini*** *to the Department of Chemistry, National Institute of Technology, Rourkela, Odisha, for the award of the degree of Master of Science in Chemistry is a record of bonafide research work carried out by her under my supervision and guidance. I am satisfied that the dissertation report has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.*

Rourkela-769008

Date:

**Dr. Priyabrat Dash**

**(Supervisor)**

# ACKNOWLEDGEMENTS

First of all, I am thankful to my guide Dr. Priyabrat Dash who untiringly assisted me in my experiment and enhanced my knowledge base by making me aware about this experiment. My training would not have been successfully completed without the firm guidance of my guide who supervised me in my experiments.

I like to thank all faculty members of the Department of chemistry, who have always inspire me to work hard and helped me to learn new concepts and experiments during my stay at NIT, Rourkela.

I would like to thank my parents for their unconditional love and support. They have helped me in every situation throughout my life, I am grateful for their support.

I would like to accord my sincere gratitude to Miss Basanti Ekka and Lipika Rout for their valuable suggestions, guidance in carrying out experiments. Finally, I would like to thank all my labmates Nilendri and Aurobinda for all fun times we had together.

Finally I would like to thank all my friends for their support and the great almighty to shower his blessing on us and making dreams and aspirations.

*Chinmayee Priyadarshini*

# Chapter-1

# INTRODUCTION

## 1.1 General introduction

The field of nanotechnology has gained great importance in the past ten years. It enables us to believe that we would have the ability to create something new that we could precisely define. The world of nanotechnology is implanting its footprint in the present decade very rapidly. Previously material science is known by the people through the utilization of natural products like rock, leathers and other things, but now material science is popularly known by the people through the metals, alloys, ceramics and fabrics. [1] However recently "nano" has become a new relevant topic in the field of material science. Here the common aspect is the size range and over the last decades many researchers have developed many new materials (nanomaterials) with unique and tunable properties. Because of such type of behaviour they have attracted significant interest in the last decade from scientific community.

Nanostructure materials are consists of single phase or multiple phase of polycrystalline solids having average size of few nanometers (1 nm = $10^{-9}$m). Generally 1-100 nm range is taken as nano-range for convention. Confinement is the basic way for the classification of nanomaterials. Bulk structures have no confinement, but nano-wells as well as nanowires show 2-D and 1-D confinement respectively.

The synthesis of nanomaterials is generally based on two approaches. Firstly, "bottom up" approach, where small building blocks are produced and assembled into larger structure. The important controlling parameters are morphology, crystallinity, particle size and chemical composition. Secondly "top down" approach, where larger objects are modified to give smaller structure.

Synthesis of nanomaterials are done based on three strategies

- Vapour-phase synthesis
- Gas-phase synthesis
- Liquid-phase synthesis

Vapour-phase synthesis involves spray pyrolysis, laser pyrolysis, flame synthesis, flame spray pyrolysis. Gas-phase synthesis occur when super saturation achieved by vaporizing material. However liquid-phase synthesis involves co-precipitation method, sol-gel processing, micro-emulsion, hydrothermal/solvothermal synthesis, microwave synthesis, sonochemical synthesis, template synthesis etc.

## 1.2 Metal oxides

Metal oxides are the most extensively studied materials and plays an important role in the field of technology, electronic and catalytic application. These are specially used for ceramic as well as semiconductor materials. The metal elements are able to form a large diversity of oxide compounds. It is an ionic compound that is made up of positive metallic and negative oxygen ion. Due to electrostatic interaction between these ions, solid ionic bonds are formed. Oxide supported nanoparticles have wide applications in the field of solid-state catalysis and it can be used to improve the selectivity and sensitivity of solid-state gas sensors. [2]

In various technological applications, oxides are basically used in the fabrication of microelectronic circuits, sensors, piezoelectric device, fuel cells. In the emerging field of nanotechnology, a goal is achieved to make nanostructures or nanoarrays having some special properties with respect to those of bulk or single particle species. Oxide nanoparticles can exhibit unique physical and chemical properties because of their limited size and a high density of corner or edge surface sites.

In case of material synthesis, change in particle size affects in three basic properties. The first one comprises the structural characteristics, known as the lattice symmetry and cell parameters. Bulk oxides are usually stable systems along with well-defined crystallographic structures. However, the surface free energy and stress is increased with decrease in particle size. The thermodynamic stability associate with size can bring changes in cell parameters and/or structural transformations. In order to display mechanical or structural stability, a nanoparticle must have a low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures.

The second one comprises the electronic properties of the oxide. In materials, the nanostructure produces quantum size or quantum confinement effects, which essentially arise from the discrete, atom-like electronic states. According to the solid state point of view these states can be considered as being a superposition of bulk-like states with a subsequent increase in oscillator strength. Electronic effect of quantum confinement on metal oxides is related to the energy shift of exciton levels and optical band gap. In case of metal oxide a redistribution of charge occur when going from large periodic structures to small clusters. [3]
The third characteristic properties of particle size are influenced by the bulk structure of the metal oxide which has wide band gap and low reactivity. [4]Average size of an oxide particle is decreased that change the magnitude of the band gap with strong influence in the conductivity and chemical reactivity.

## 1.3 Porous hollow metal oxides

In recent years, the material scientists developed a number of ways for designing of inorganic nanomaterials which has specific nanomorphologies as well as unique physical and chemical characteristics. Inorganic nanomaterials are having the shape and size dependent properties. [5, 6] Over the past years, hollow metal oxide nanostructures have attracted much more interest because of their well-defined morphology, large surface area, low density, high surface-to-volume ratio, uniform size, refractive index and widespread potential applications. [2, 7] These are lightweight material because of their porous structure.

The function of hollow metal oxides are, they can act as small container for encapsulation to control the drug delivery and to protect the environment and also for sensitive materials such as catalyst, coating, pigment, enzyme and so on. [8] The design and fabrication of hollow nanospheres or nanostructures has made great strides over the past decades. [9] Metal oxide hollow spheres normally synthesized by use of polymers, inorganic non-metals, metal-based hard templates, small-molecule emulsion, surfactant micelle-based soft-templates, and the template free approach. [2] Particularly for hollow micro or nanospheres, the template based colloidal particle is more common. The templates used for synthesis of hollow spheres are of two types such as hard template and soft template. The hard template can be of various compositions like silica, polymer and carbon particle and the soft template are micelles, emulsions and so on. [10] However hard template-free synthetic method is widely applicable for the synthesis of porous and hollow microspheres which have attracted more considerable interest. It is a challenging factor for the construction and controlling of nanostructures based on the properties of porous and hollow microspheres. [11] Semiconductors have great significance in the field of material science for the preparation of hollow metal oxides. The aim is to control the morphology of various nanostructures due to shape and size dependent properties.

In the following section much attention has concentrate on the material synthesis based on hollow ZnO and $SnO_2$ due to their various potential applications. The two metal oxides (ZnO and $SnO_2$) are used for sensor applications. ZnO is a versatile material and n-type semiconductor having wide band gap (3.37 eV) and its exciton binding energy is large (60 meV) at room temperature. [12] This metal oxide has attracted increasing attention because of their unique electrical and optical properties as well as various potential applications towards optical wave guides and solar cells. It is used as photocatalyst and has sensor applications. It is sensitive to ethanol, carbon monoxide and acetone and is environmentally benign. Many

researchers investigate the synthetic method for the preparation of zinc oxide based on shape-dependent optoelectronic and gas sensing properties. [12, 13] Hollow ZnO microstructures have attracted considerable interest because of their low density and high surface area.

Tin oxide ($SnO_2$) is an n-type semiconductor having wide band gap (3.6 eV). It has various properties such as high electrical conductivity; high transparency in the visible region and high thermal, chemical and mechanical stability. Porous $SnO_2$ metal oxide can act as anode material for lithium-ion batteries due to higher theoretical capacity as well as reversible alloying/de-alloying reaction between $Li^+$ and Sn. It is found to show gas sensing properties. [14]

**1.4 Novel ionic liquid is a suitable media for the hollow metal oxides**

Ionic liquid (IL) assisted inorganic material synthesis represents a new research direction in the field of material chemistry and initiates the new generation of chemical nanostructures. [15] An ionic liquid is a salt in which the ions are poorly coordinated and it is liquid below100$^{\circ}$C or even at room temperature. It consists of ionic species such as cation and anion. One ion has a delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice. It is very viscous in nature. The room temperature ionic liquid (RTIL) is the class of IL which is free-flowing liquid at ambient temperature (25°C). It is colourless and easy to handle. Ionic liquid is generally the salt of organic cations, e.g., tetraalkylammonium, tetraalkylphosphonium, N-alkylpyridinium, 1, 3-dialkylimidazolium and N-alkylpyrrolidinium etc. The most important aspect of the room temperature ionic liquids are that they form hydrogen bond system in the liquid state so they are very helpful for the self-assembly of nanoscale structures.

Room temperature ionic liquids are environmentally benign solvents; has generated much attention towards organic chemical reactions. The unique features of ionic liquids (ILs) are that have excellent characteristics of negligible vapour pressures, good thermal stability, high ionic conductivity, broad electrochemical potential windows as well as high thermal stability. [16, 17] These characteristics made them novel environmentally friendly solvent, used for enzyme catalyzed reactions as well as in photochemical solar cells and in electrochemical devices. [18] ILs have wide liquid range due to their low melting points (as low as -80$^{\circ}$C) and high thermal stability (stable below 300$^{\circ}$C). For the last few years, ILs have focused on templates or cosolvent systems especially for the fabricated nanostructured inorganic materials. Due to solvent properties, it is the more convenient way for the ILs to interact with

various surface and chemical reaction environments. [15] Generally1-alkyl-3-methylimidazolium salts are the common ionic liquids due to their air and moisture stability. Ionic liquids have various physicochemical properties such as viscosity, solvation dynamics, catalytic activity, melting point and hydrophobicity nature. These properties of ionic liquids depend on cation, anion and length of the alkyl group. ILs is the suitable solvents for the inorganic, organic and polymer materials due to wide range of liquids. In recent years ILs are the most advance solvent for the inorganic nanomaterials syntheses and has unique physical and chemical properties.. Till now the synthesis of hollow metal oxides in ionic liquids, their functionalization by noble metal nanoparticles and their catalytic as well as sensing application has not been studied so far. [19]

Ionic liquids are salt that liquid at room temperature, for example Imidazolium based ionic liquids. ILs has attracted great attention towards the reaction media generally for the organic synthesis. Recently, ILs has attracted great deal of interest for the fabrication of inorganic materials with various potential applications. It is very improbable factor that all the organic solvents or aqueous systems or gas phase processes will be replaced by the ionic liquids for the fabrication of inorganic materials. The reaction in ionic liquid takes short period of time and occurs under milder conditions than the reaction in other solvents in inorganic materials. Because ionic liquids have some definite properties, act as very efficient and chemically simple. It is all-in-one systems for the advanced material synthesis. In the reaction media ILs act as template and also stabilise the structure which is formed. In some cases, IL can act as solvent-template reactant in which it is noticed that the inorganic materials formed in IL not only interact with the chemical structure but also they are the part of the reaction media in inorganic material synthesis. Recently much investigation is carried on the effect of IL on crystallization. Their nucleation energy is low and they also have an impact on the polymorphs of inorganic materials. [1]

Hollow metal oxide spheres are generally synthesized by employing various methodologies, such as use of polymers, inorganic non-metals, and metal-base hard and soft templates. Template method is the most common for the synthesis of hollow metal oxide. Two steps are involved for the method. First, the template must be changed to give inorganic precursors such as salts or alkoxide onto the surface of the template core. Then the template must be eliminated by heating method after the inorganic shell is decorated outside the scaffold, leaving behind a hollow shell. [2] In the following section, the hollow ZnO and $SnO_2$ spheres are synthesized by using different methods of ionic liquid solvents and non-ionic liquid solvents. The large scale self-assembly route for the hollow ZnO nanospheres were

studied by Mo et al. [5] The ZnO nanosheets were self-assembled to form hollow ZnO spheres by the process of hydrothermal thermolysis of zinc ethylenediamine derived complex precursor in presence of water soluble poly(sodium-4-styrenesulfonate) polymer. Sol-gel technique is most popular for the synthesis of hollow ZnO nanospheres. Zhang *et al.* has described the fabrication of hollow ZnO nanospheres by applying sol-gel reaction using carbon template. [20] When $Zn^{+2}$ (zinc acetate) ion adsorbed on the surface of the template (carbon nanospheres), the core/shell structure was formed. Further it undergo calcination give rise to hollow ZnO nanospheres.

Gang *et al*. reported a novel simple method for the synthesis of porous ZnO hollow spheres. They described the synthesis strategy depend upon oxidizing Zn spheres and polyhedrons in solid state. The Zn spheres and the polyhedrons together form a ZnO layer on the surface at very low temperature. The removal of Zn cores upon heating led to the formation of ZnO hollow spheres. [21]

Iionic liquids are used for the synthesis of inorganic materials because of their tuneable solvent properties, high thermal stability and negligible vapour pressure [15] In this section the ZnO [22, 23] and $SnO_2$ [24, 25] are described briefly. Zhou *et al.* reported the synthesis of flowerlike ZnO with interesting morphology by using a new series of ionic liquids $(Zn(L)_4(NTf)_2)$ in which L = alkylamine and $NTf_2 = N(SO_2CF_3)_2$. [26] Wang *et al.* described the synthetic procedure of needle like and flowerlike ZnO nanostructure by the heating method of an aqueous solution of $Zn(NO_3)_2$ and NaOH. [24]

Taubert and co-workers reported ZnO mesocrystals by using an ionic liquid precursor (Tetrabutylammonium hydroxide). [27, 28] Metal oxide microspheres have attracted great interest in research field. It is very difficult to control and construct the nanostructure which plays an important role in the case of microspheres and hollow microspheres. Zhang *et al.* synthesized ZnO microsphere and hollow microsphere by using immidazolium tetrafluoroborate ionic liquid with different alkyl chain length. [11] Xia and co-workers synthesized $SnO_2$ hollow sphere by sol-gel method in which sol-gel precursor is templated against the monodispersed polycrystalline beads. [29] Zhao *et al.* synthesized $SnO_2$ hollow spheres by making a micelle system which is made up of the surfactants tetraphtalic acid along with sodium dodecyl benzene sulfonate (SDBS) in ethanol and water medium. [30] The aqueous solution of sucrose and $SnCl_4$ undergo hydrothermal reaction to prepare the multi-layered $SnO_2$-carbon composite (self-assembly) and after the removal of carbon component $SnO_2$ hollow microsphere is obtained, which is reported by Yang *et al.*[31] Kirkendal effect plays a vital role in the material synthesis especially for hollow metal oxides. [32] According

to the Kirkendal effect hollow structures can be developed only when the outward diffusion of metal cations in the oxide shell layer is very fast than the inward diffusion of the oxygen to the metal core. Gaiduk *et al.* follow the Kirkendal effect mechanism to form $SnO_2$ hollow spheres by changing the heat treatment temperatures and the partial pressure of oxygen. [33] Liu and co-workers prepared rutile structure of $SnO_2$ microsphere having average diameter 2.5 μm by hydrothermal microwave heating using 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid. [25] Yan and co-workers reported nanocrystalline porous $SnO_2$ by sol-gel method using 1-hexadecyl-3-methylimidazolium bromide ionic liquid as a template. [26] This is totally based on ionic liquid mediated inorganic material synthesis having different structure and morphology.

**1.5 Structural properties of metal oxides**

Generally the crystal structure of ZnO is of two types such as hexagonal wurtzite structure and cubic zinc blende structure. The ZnO having wurtzite structure only when there is optimum pressure and temperature and it is thermodynamically stable. [22, 34] It has hexagonal closed-packed lattice type with lattice parameters, a=0.32495 nm and c=0.52069 nm, in the ratio of c/a=1.602 and the space group is P63mc. [22, 35] Again this is characterized by two interlink sub lattices ($Zn^{2+}$ and $O^{2-}$). Each anion of the structure is surrounded by four cations at the corners of a tetrahedron with $sp^3$ covalent bonding. The closed-packed planes are ABAB type. The zinc blende has the closed-packed planes ABCABC type. Zinc blende phase is unstable and when the crystals become bigger it transforms into wurtzite structure. The wurtzite structure of ZnO and the zinc blende structure of ZnO are shown in Fig. 1.

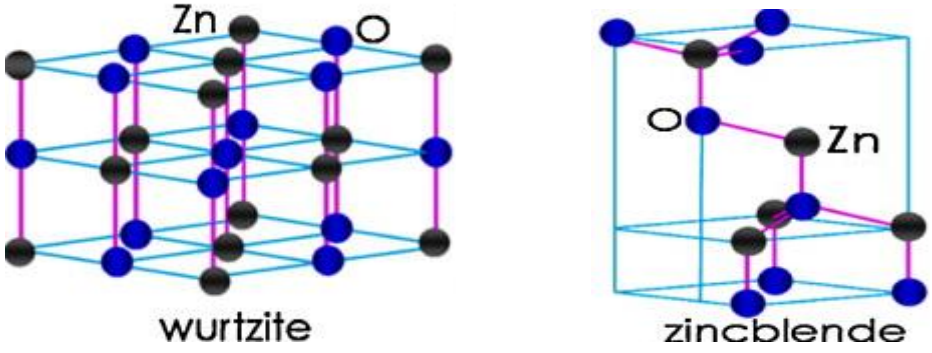


**Fig. 1: Wurtzite and Zinc blende structure of ZnO. [15]**

Due to versatile and multifunctional characteristic of ZnO is well known in research field, so various synthetic techniques are developed in which ZnO formed with different novel nanostructure. The wide band gap makes enable ZnO to form different nanocrystals structure.

The $SnO_2$ metal oxide is an n-type semiconductor and having rutile structure. The unit cell is tetragonal and having two Sn (octahedral coordinated) and four O (trigonal planer coordinated) in each unit cell. The ratio of Sn and O is 1:2. The lattice parameter a=4.584 Å and c=2.959 Å, is in the ratio of c/a=0.673. The rutile structure is shown in Fig. 2. The band gap energy is high (3.0 eV). Due to low cost and highly stable in water it is widely applicable. [36]

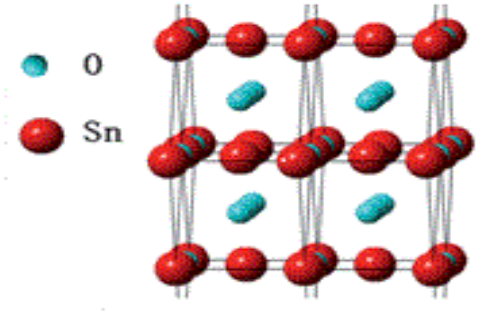


**Fig. 2: Rutile structure of $SnO_2$ microsphere.** [36]

As described above ionic liquid has been suitable solvent for inorganic material syntheses because of their air and water stability and wide liquid range. In this work we used $BMIMPF_6$ (1-butyl-3-methylimidazolium hexafluorophosphate) as a novel media for the preparation of zinc oxide nanoparticle and zinc oxide hollow microsphere. It is a colourless, viscous, hydrophobic and non-water soluble ionic liquid. The main purpose of the use of ionic liquid is that it has the capacity to control the nanostructure and morphology of spheres and hollow spheres as soft templates.

### 1.6 Objectives of the present study

The main research objectives of the present study are:

- To synthesize, purify and characterize $BMIMPF_6$ ionic liquid.
- To synthesize hollow metal oxides (ZnO and $SnO_2$) in ionic liquids by techniques such as sol-gel synthesis and hydrothermal treatment.
- To characterize the above metal oxides by XRD and SEM.
- Photoluminescence behaviour will be studied to follow the evolution of metal oxide size and metal oxide structure.

# Chapter-2
# MATERIALS AND METHODS

## 2.1 Materials

1-methylimidazole (99%) and 1-chlorobutane (99.5%) was purchased from Sigma-Aldrich and was distilled over KOH and $P_2O_5$, respectively. Hexafluorophosphoric acid (ca. 65% solution in water), zinc nitrate and zinc acetate, all were purchased from Aldrich. Sodium hydroxide, ethanol and methanol were purchased from Himedia. Ethylene glycol (99%), tin (IV) tetrachloride pentahydrate, resorcinol and formaldehyde solution were purchased from Sigma-Aldrich. Milli-Q water (Millipore, 18 MΩ) was used throughout.

## 2.2 Ionic liquid assisted synthesis of Zinc oxide nanoparticle

### 2.2.1 Synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) ionic liquid

Before synthesis of $BMIMPF_6$, we have to synthesize BMIMCl. To a 100 ml round bottom flask 1-methylimidazole (1.0 mol) was added in toluene (100 $cm^3$) at 0 °C in vigorously stirred condition. After 5 min stirring, 1-chlorobutane (1.1 mol) was added and the solution was heated to reflux at 80 °C for 72 h under nitrogen atmosphere. The solution mixture was two phase layer one is the layer of BMIMCl and the other layer is toluene. Toluene was decanted. After toluene separation a crystalline solid of BMIMCl was obtained. Then the resulting product was recrystallized with acetone several times. Finally the resulting product was obtained. NMR was taken to check its purity and is shown in Fig. 3. $^1$H-NMR($CDCl_3$, 400MHz): δ(ppm) = 10.52 (s, 1H, NCHN), 7.58 (m, 1H, $CH_3NCHCHN$), 7.43 (m, 1H, $CH_3NCHCHN$), 4.32 (t, 2H, $NCH_3(CH_2)_2CH_3$), 4.09 (s, 3H, $NCH_3$), 1.82 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.35 (m, 2H, $N(CH_2)_2CH_2CH_3$), 0.94 (t, 3H, $N(CH_2)_3CH_3$).

In a typical synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate, BMIMCl (0.17 mol) was transferred to round bottom flask followed by the addition of 40 ml of deionised water. An aqueous solution of 65% $HPF_6$ in a 1.1:1 molar ratio was added slowly to minimise the amount of heat generated As $HPF_6$ was added two phases formed, where $BMIMPF_6$ was the bottom phase and the HCl was the upper phase. The upper phase was decanted and the remaining product was washed with water several times. Then the resulting product was dried at 70 °C in vacuum line for 4 h to get the desired product. NMR spectra were shown in Fig. 4.$^1$H-NMR($CDCl_3$, 400MHz): δ(ppm) = 8.29 (s, 1H, NCHN), 7.258 (d,

1H, $CH_3NCHCHN$), 7.22 (d, 1H, $CH_3NCHCHN$), 4.05 (m, 2H, $NCH_2(CH_2)_2CH_3$), 3.78 (s, 3H, $NCH_3$), 1.71 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.25 (m, 2H, $N(CH_2)_2CH_2CH_3$), 0.816 (t, 3H, $N(CH_2)_3CH_3$).

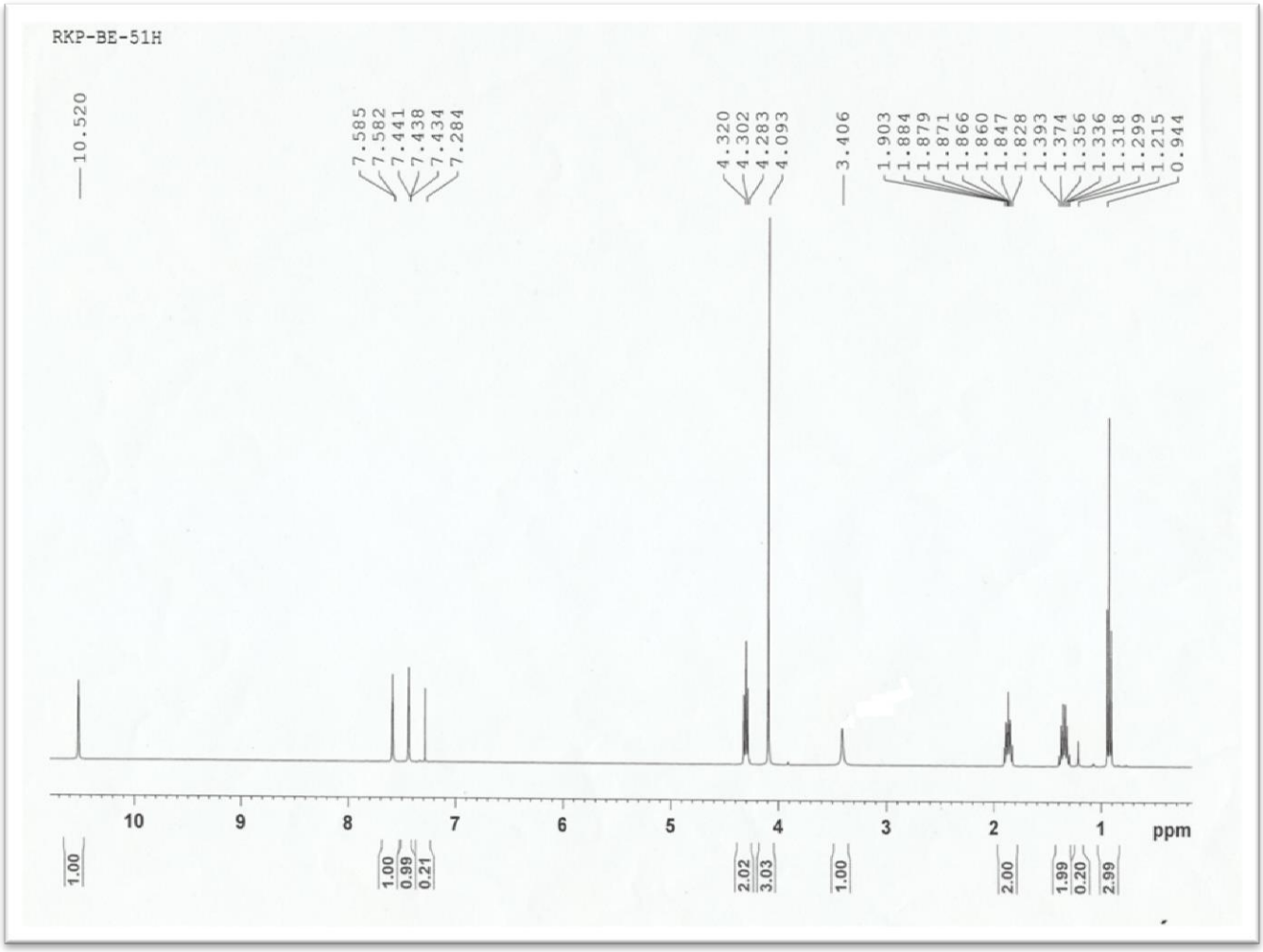


**Fig. 3: NMR spectra of 1-butyl-3-methylimidazolium chloride.**

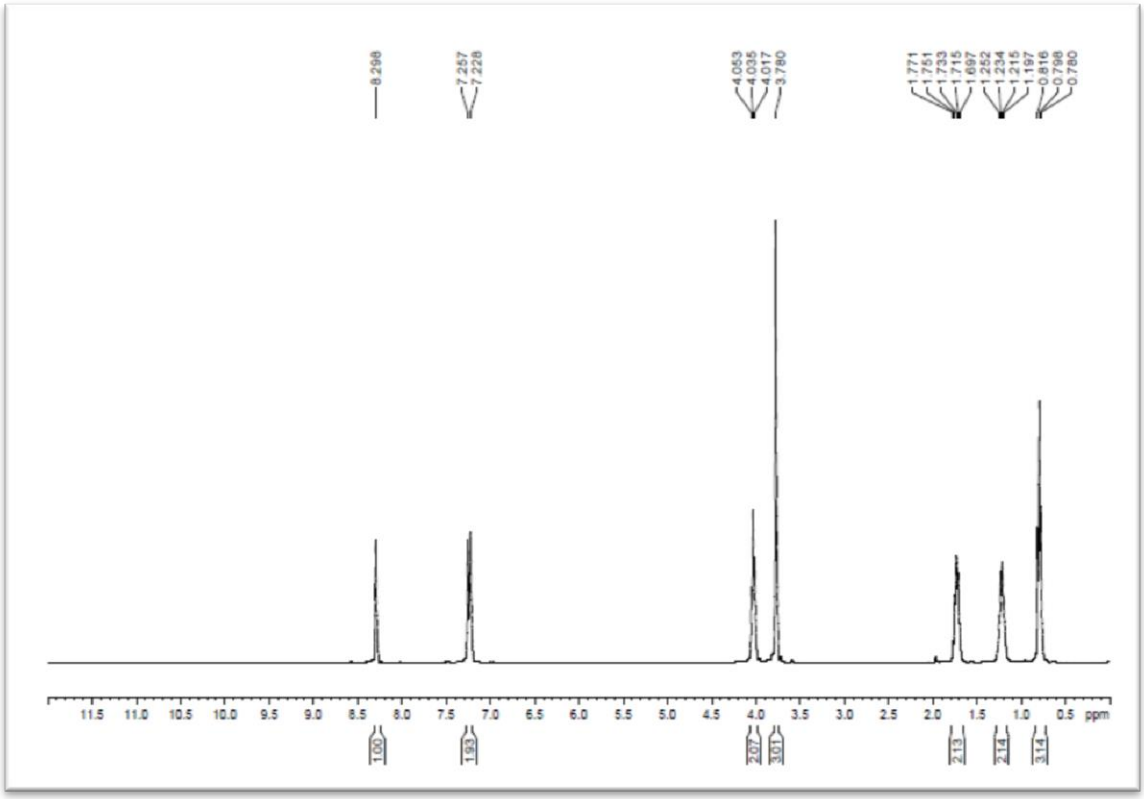


**Fig. 4: NMR spectra of 1-butyl-3-methylimidazolium hexafluorophosphate.**

### 2.2.2.. Preparation of Zinc oxide nanoparticle with $BMIMPF_6$

About 0.439 g of zinc acetate (2 mmol) was grounded in agate mortar for 5 min. Then 0.35 g $BMIMPF_6$ (2 mmol) and 0.24 g NaOH (6 mmol) flake was added to it and grounded for 50 min to get a white batter. It was washed with distilled water and ethanol several times to remove the ionic liquid and then dried in vacuum at 60 °C to get ZnO nanoparticle.

### 2.3 Synthesis of Zinc oxide hollow microsphere in ionic liquid

About 3 g of zinc nitrate (10.1 mmol) was dissolved in 35 ml of ethylene alcohol and 5 ml of 1-butyl-3-methylimidazolium hexafluorophosphate (as synthesized by above procedure) was added. The mixture was stirred for 24 h to form a clear solution. After getting the clear solution, it was transferred to autoclave. The reaction temperature was 180 °C. The resultant products were collected by centrifugation and then washed with distilled water and ethanol to remove ionic liquid and dried at 80 °C in a vacuum oven to get ZnO microsphere. For further characterization it was annealed at 500 °C.

### 2.4 Synthesis of hollow tin dioxide microsphere in ionic liquid

The 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid was synthesized as above the procedure. 2 g of tin (IV) tetrachloride pentahydrate (5.7 mmol) was dissolved in 13.3 ml methanol and 3.8 g ionic liquid (13.3 mmol). Then the methanol was separated by the mixture by using schlenk line. After removal of methanol 0.85 g of resorcinol and 1.27 ml formaldehyde was added to the solution. Then the resulting mixture was aged at 85 °C for 3 h to getting a $SnCl_4$/resorcinol-formaldehyde (RF) gel composite. It was calcined at 400 °C for 1 h to produce the hollow $SnO_2$ microspheres.

### 2.5 Characterization of metal oxides

The materials synthesized in above sections were characterized by X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), UV-Visible spectroscopy (UV-Vis), Infra-Red Spectroscopy (IR). To check purity of ionic liquid, NMR was taken.

**UV-Vis Spectroscopy**

UV-Vis Spectra of pure ionic liquid $BMIMPF_6$ were recorded by Shimadzu spectrophotometer (UV-2450) in the range of 200-900 nm.

**X-ray diffraction (XRD)**

The X-ray diffraction patterns of the ZnO and $SnO_2$ samples were recorded on a Philips PAN analytical diffractometer using Ni-filtered $CuK_{\alpha 1}$ radiation. The XRD measurements were carried out 10-80 °C and 30-70 °C for $SnO_2$ and $ZnO_2$, respectively with a scan speed of 3 degrees per minute.

**Scanning Electron Microscopy (SEM)**

Scanning electron microscopy was taken using JEOL JSM-6480 LV microscope (acceleration voltage 15 kV). The sample powders were deposited on a carbon tape before mounting on a sample holder for SEM analysis.

**Infrared Spectroscopy (IR)**

The IR spectra of ZnO nanoparticle (as KBr pellets) were recorded using Perkin-Elmer infrared spectrometer with a resolution of 4 $cm^{-1}$, in the range of 400 $cm^{-1}$ to 4000 $cm^{-1}$. Nearly 3-4 mg of the sample was mixed thoroughly with 30 mg of oven dried KBr and made into pallets.

**Nuclear magnetic resonance (NMR) spectroscopy**

Since ionic liquids are predominantly used as solvents so it is necessary for the application of nuclear magnetic resonance spectroscopy to check the purity of the ionic liquids. NMR was taken on a 400 $MH_Z$ Bruker instrument.

**Photoluminescence spectra**

The emission spectra and steady state fluorescence anisotropy values were recorded using Horiba Jobin Yvon Spectrofluorometer (Fluoromax~4P).

# Chapter-3

# Results and Discussion

### 3.1 UV-Vis study

Ionic liquid is synthesized as mentioned above. The UV-Vis spectra of the pure ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate), in the scanning range 200-800 nm are shown in Fig. 5. To minimise the effect of impurities on ionic liquid, it was washed with water. In order to see whether colored impurities were still present or not, UV-Vis spectra were taken. No absorption peak is observed that confirmed colourless impurity free ionic liquid.

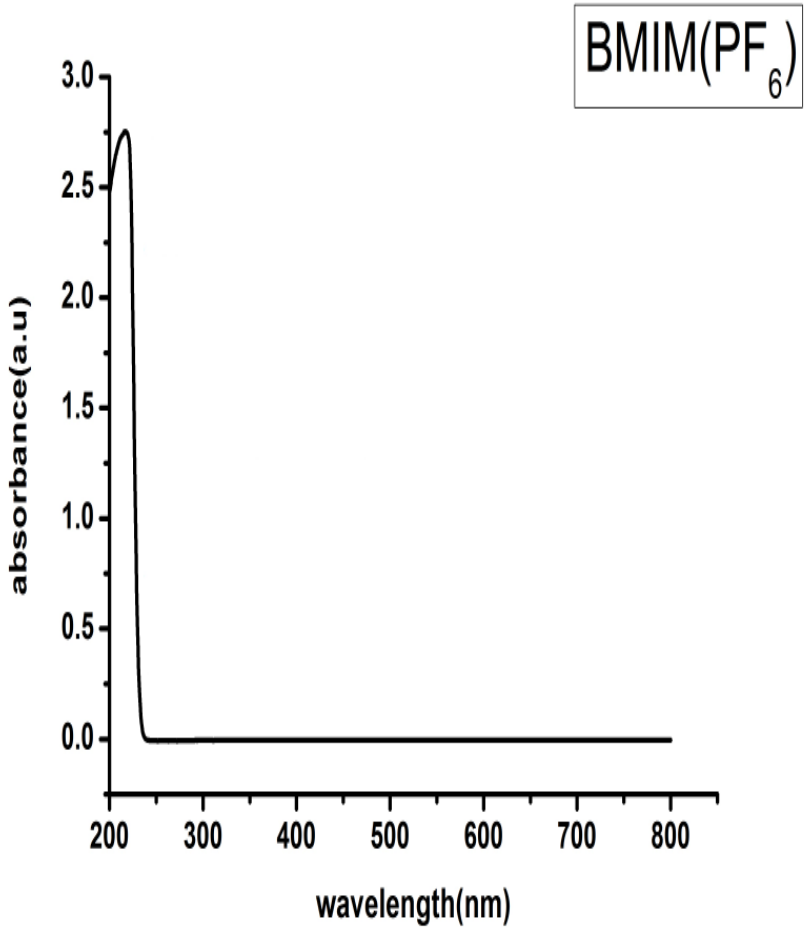


**Fig. 5: UV-Vis spectra of 1-butyl-3-methylimidazolium hexafluorophosphate.**

### 3.2 XRD study

Fig. 6 shows the powder XRD pattern of the zinc oxide nanoparticle prepared by using 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid.

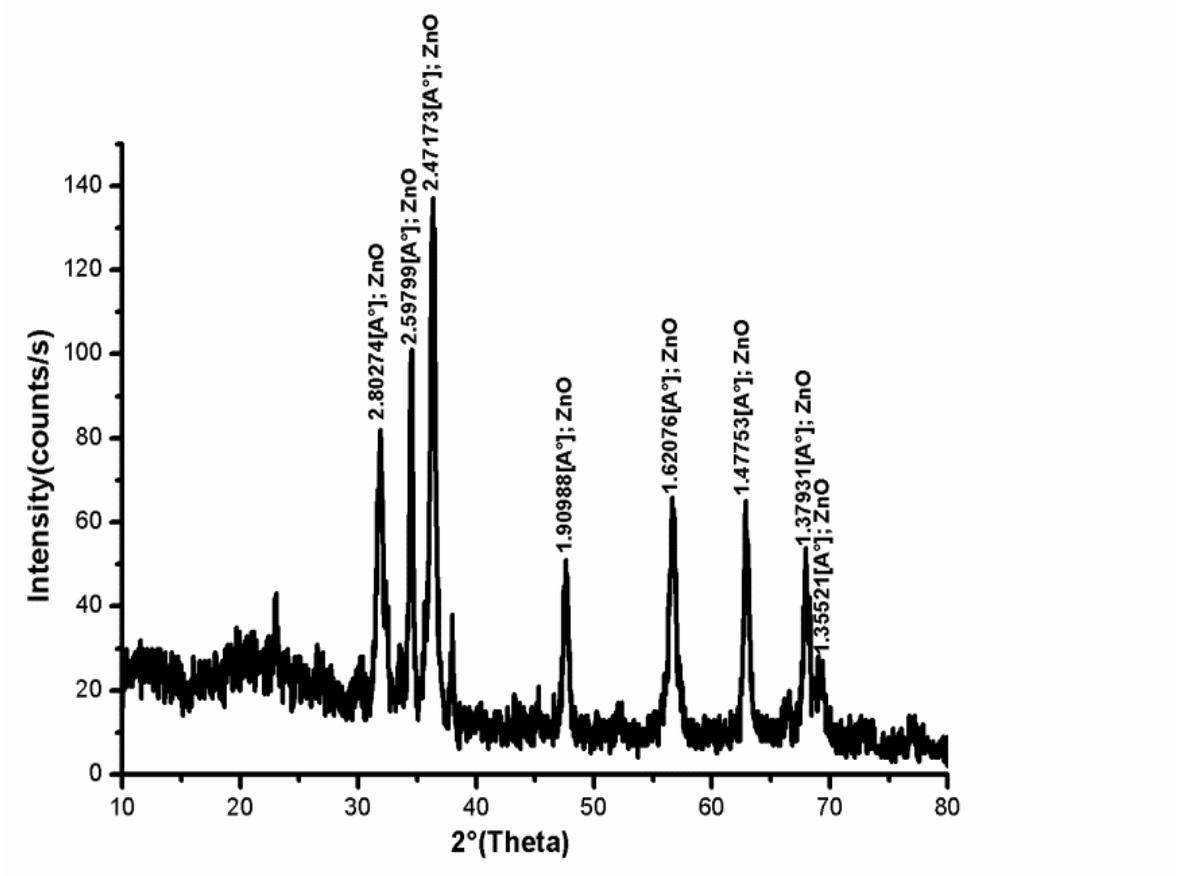


**Fig. 6: XRD pattern of ZnO nanoparticle in $BMIMPF_6$.**

The crystal structures of the materials were characterized using XRD. The pure zinc oxide (ZnO) nanoparticle shows XRD pattern with 2θ value at 36.3 degree. All the peaks correspond to the presence of the hexagonal wurtzite structure (JCPDS-790206). No other characteristic peaks are observed for impurities like $Zn(OH)_2$.

Fig. 7 shows the XRD pattern of zinc oxide microspheres with ionic liquid after annealation at 500 °C.

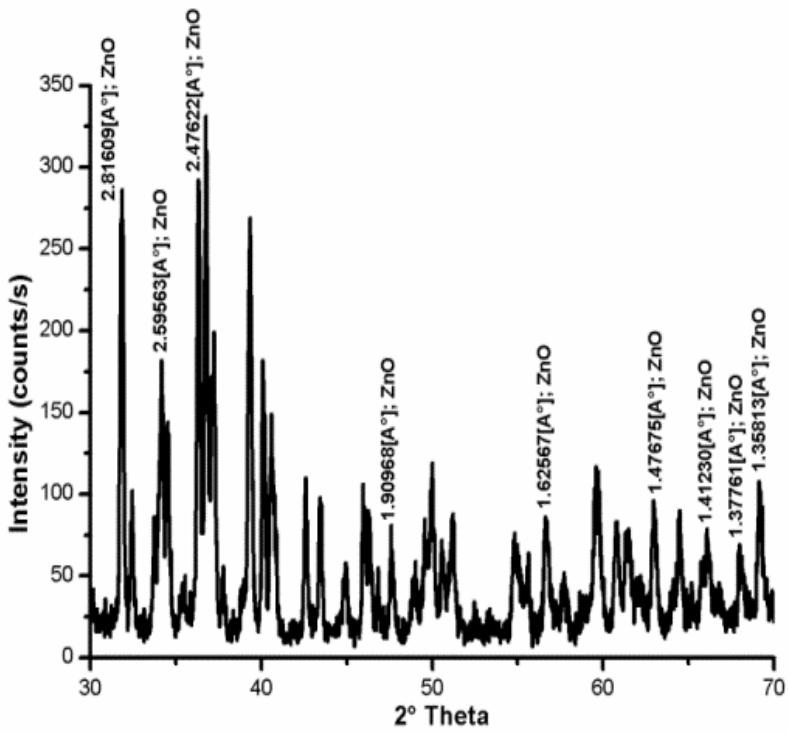


**Fig. 7: XRD pattern of ZnO microsphere after annealing.**

The phase analysis of the products is carried out using an X-ray diffractometer. However in the case of ionic liquid-controlled synthesis of ZnO microsphere, data are collected in the 2θ range of 30° to 70°. All the peaks indicate the presence of wurtzite-type structure after annealing at 500 °C. Fig. 6 shows the XRD pattern of ZnO microsphere in presence of ionic liquid after annealation (JCPDS file No. 74-1816). In the present reaction system zinc nitrate was used that resulted a lower pH value. XRD pattern of ZnO microsphere shows ZnO along with other peaks like zinc phosphate. As the reaction mixture was left for three days before analysis, it oxidised with air and because of that reason it formed ZnO zinc phosphate might have formed along with ZnO.

In the case of tin dioxide microsphere, the $SnO_2$ phase started to appear after heat treatment at 400 °C in air. Fig. 8 shows the XRD pattern of $SnO_2$ microspheres in the 2θ range of 10°-70°, which was produced after direct air-oxidation of the $SnCl_4$/RF gel composite.

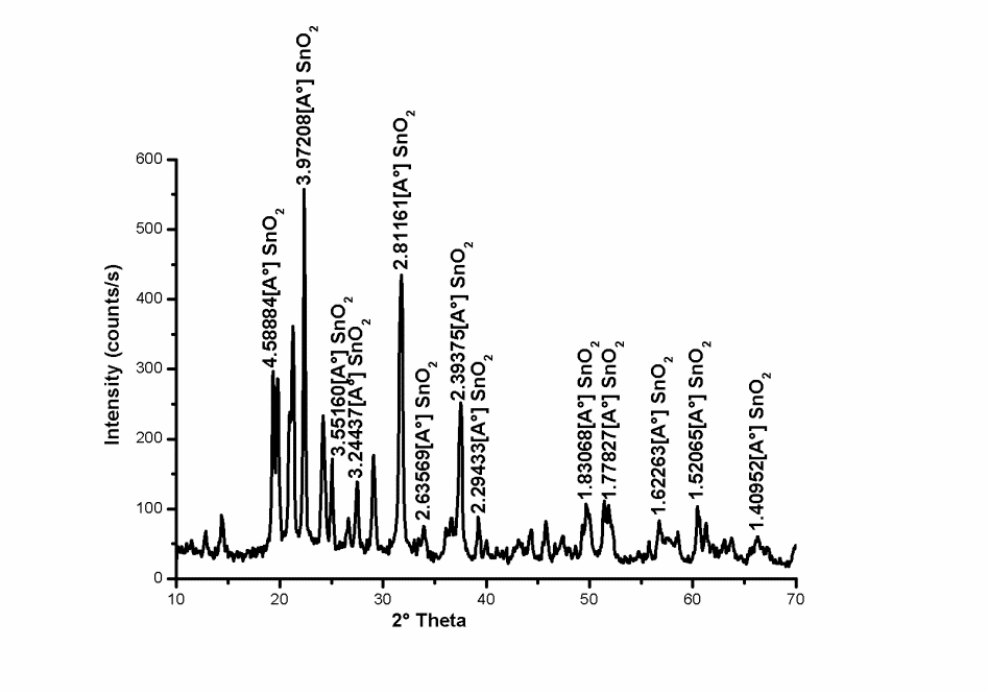


**Fig. 8: XRD pattern of $SnO_2$ microsphere.**

### 3.3 FTIR study

The FTIR spectrum of pure ZnO nanoparticles synthesized by one-step solid state reaction was analysed in the spectral region 400-4000 $cm^{-1}$. Fig. 9 shows the FTIR spectrum of the ZnO nanoparticles. From FTIR we can observe the crystalline nature of ZnO. The peaks in the range of 1400-1500$cm^{-1}$ corresponds to the C=O bonds. The peaks in the range of 500-1000 $cm^{-1}$ correspond to the Zn-O stretching mode and from 1150-1200 $cm^{-1}$ is due to tertiary alcohol (O-H). The band considering at 2400-3200 $cm^{-1}$ shows the N-H bonds. This may be arising due to the presence of imidazolium ionic liquid.

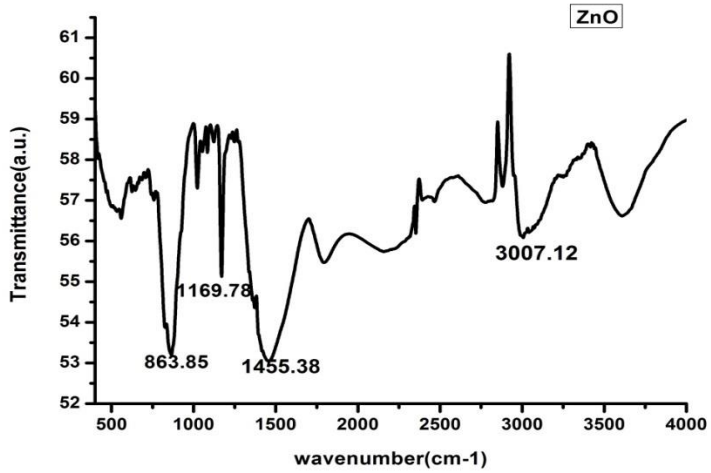


**Fig. 9: FTIR spectra of ZnO nanoparticles.**

### 3.4 Photoluminescence study

Fig.10 depicts the room temperature photoluminescence spectra of ZnO nanoparticle. The excitation wavelength is 325 nm. There is a strong and broad light emission around 562 nm, which comes from the recombination of electrons in singly occupied oxygen vacancies with photo excited holes.

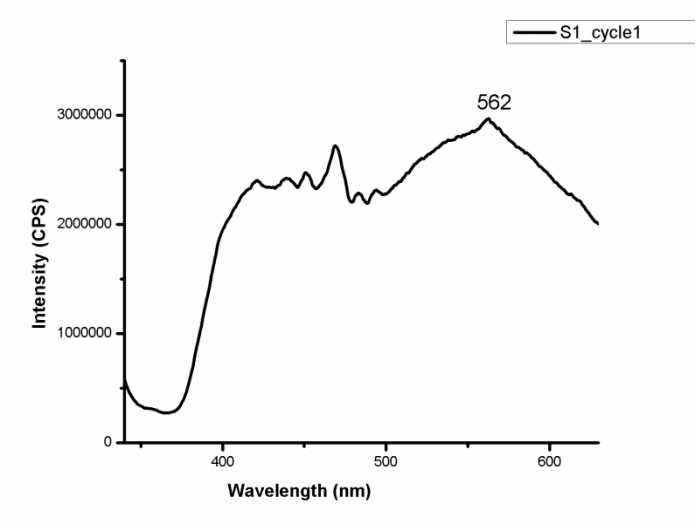


**Fig. 10: Photoluminescence spectra of ZnO nanoparticle.**

### 3.5 Scanning electron microscopy (SEM)

Fig. 11 shows the SEM micrograph of the synthesized ZnO microsphere with a diameter of 1.5 ± 2 μm. It demonstrates clearly the formation of spherical ZnO microspheres with high degree if homogeneity. The particle size was calculated by the software ImageJ.

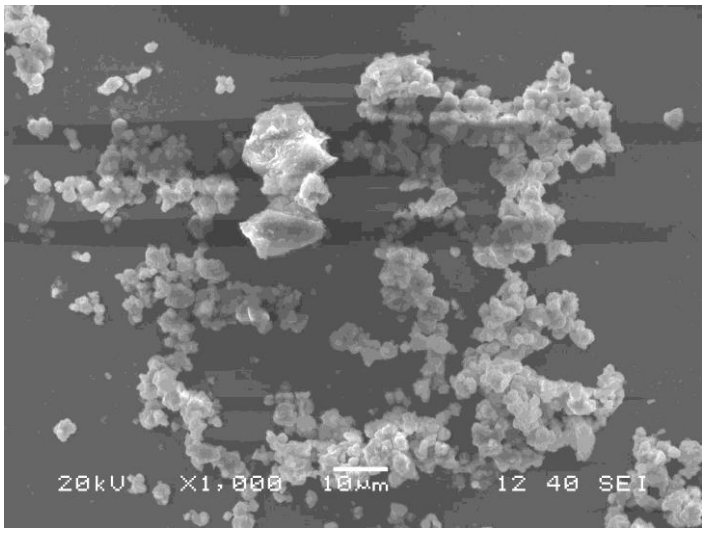


**Fig. 11: SEM image of ZnO microspheres**

The morphology of $SnO_2$ microspheres derived from solvothermal reaction of resorcinol-formaldehyde (RF) gel composite in the presence of $BMIMPF_6$ was characterized by SEM.

As can be seen from Fig. 12, the product mainly consists of microspheres with small polydispersity, having an average 0.6 μm in diameter. The SEM image of $SnO_2$ microspheres confirms that the microspheres are solid.

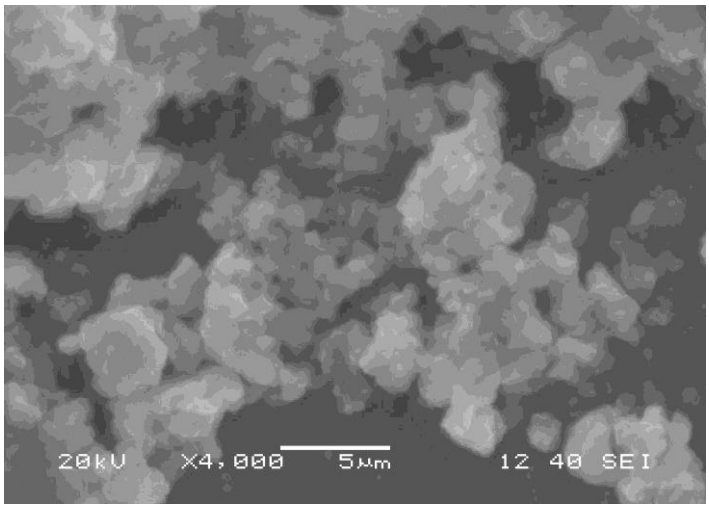


**Fig. 12: SEM image of $SnO_2$ microspheres.**

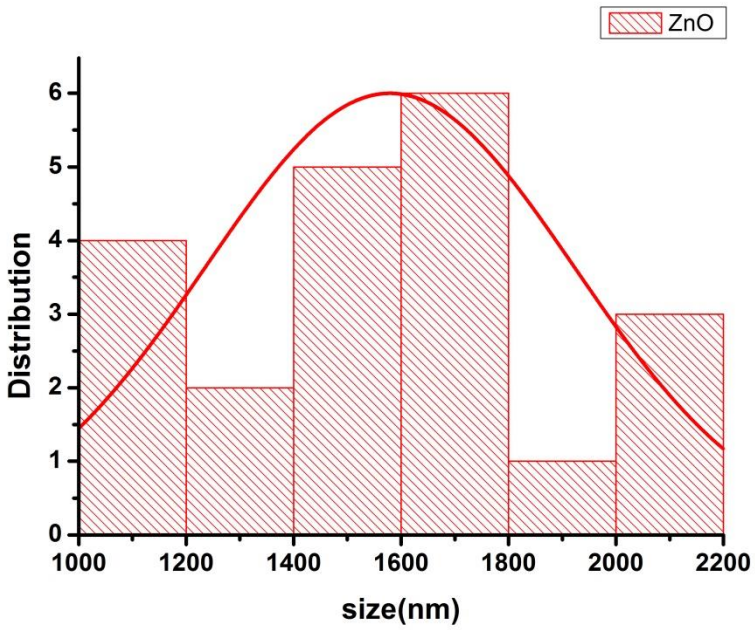


**Fig. 13: Histogram of ZnO microspheres.**

Fig. 13 indicates the histogram of the zinc oxide microspheres as synthesized by using 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. The average particle size was found to be 1.5 μm (±2 μm).

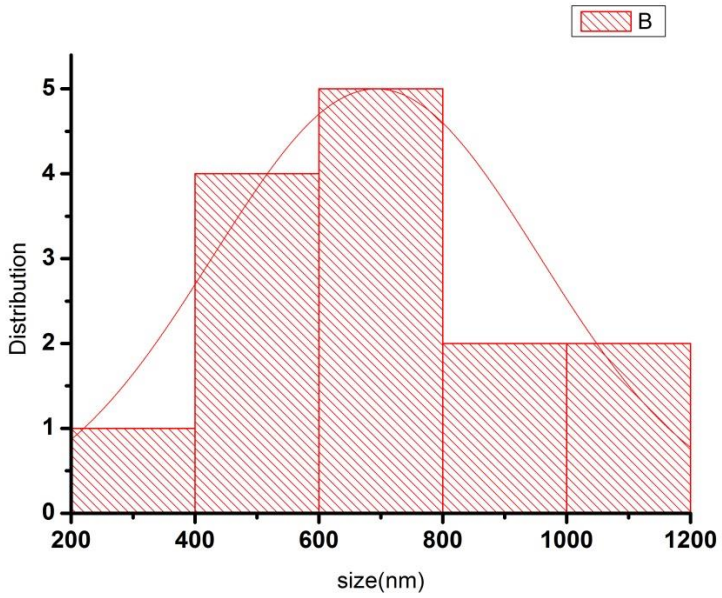


**Fig. 14: Histogram of $SnO_2$ microsphere.**

Fig. 14 indicates the histogram of $SnO_2$ microspheres. The average particle size was found to be 0.6 μm.

# Chapter-4

# CONCLUSION

The one-step solid state reaction and the solvothermal reaction tuned by ionic liquid have been successfully explored as effective methods for the synthesis of ZnO nanoparticles, ZnO microspheres and $SnO_2$ microspheres. These microstructures might bring about various changes in the properties of materials. The SEM results showed that the formation of spherical shaped microsphere in case of ZnO microspheres and solid microspheres in case of $SnO_2$ microspheres. XRD study indicates the crystal structure of the materials. This was further confirmed from FTIR study, where a sharp absorption band related to Zn-O vibration band was noted. The synthesis of materials with ionic liquids provides a really facile approach, not only for different hierarchical nanostructures but also beneficial for the design of new functional nanostructured materials.

# References


**1.** Taubert, A. *Acta Chim. Slov.* **2005**, 52, 183.

**2.** Hu, J.; Chen, M.; Fang, X.; Wu, L. *Chem. Soc. Rev.***2011**, 40, 5472.

**3.** Moriarty, P. *Rep. Prog. Phys.* **2001,** 64, 297.

**4.** Rodriguez, A. R. *Theor. Chem. Acc.* **2002**, 107, 117.

**5.** Zhonghao, L.; Zhen, J.; Yuxia, L.; Tiancheng, M. *Current Opinion in Solid State and Materials Science* **2008**, 12, 1.

**6.** Zhengquan, L.; Yi, X.; Yujie. X.; Rong, Z. *New J. Chem.* **2003**, 27, 1518.

**7.** Cheng, S.; Yan, D.; Chen, J. T.; Zhuo, R. F.; Feng, J. J. *J. Phys. Chem. C* **2009**, 113, 13630.

**8.** Sulieman, K. M.; Huang, X.; Liu, J; Tang, M. *Nanotechnology*, **2006**, 17, 4950.

**9.** Haisheng, Q.; Guofeng, L.; Yunxia, Z.; Poernomo, G.; Rong, X. *Nanotechnology*, **2007,** 18, 355602.

**10.** Maria, M. T.; Markus, A.; Arne, T. *Chem. Mater.* **2006**, 18, 3808.

**11.** Zhang, J.; Wang, J.; Zhou, S.; Duan, K, Feng, B. *J. Mater. Chem.* **2010**, 20, 9798.

**12.** Zhonghao, L.; Qian, Y.; Yuxia, L. *CrystEngComm.* **2009**, 11, 2683.

**13.** Wang, L.; Lou, Z.; Fei, T.; Zhang, T. *J. Mater. Chem.* **2011**, 21, 19331.

**14.** Chen, Y.; Ma, J.; Wang, T.; Li, Q. *CrystEngComm.* **2012**, 14, 6170.

**15.** Arya, S. K.; Saha, S.; Gupta, V.; Singh, S. P. *Analytica Chimica Acta* **2012**, 737, 1.

**16.** (a) Ma, Z.; Yu, J.; Dai, S. *Adv. Mater.***2010**, 22, 261. (b) Torimoto T.; Tsuda, T.; Okazaki, K.-I.; Kuwabata, S, *Adv. Mater.***2010**, 22, 1196.

**17.** Plechkova, N. V.; Seddon, K. R. *Chem. Soc. Rev.* **2008**, 37, 123.

**18.** Parvulescu, V. I.;Hardacre, C. *Chem. Rev.***2007**, 107, 2615.

**19.** Ge, L.; Wang, J.; Jamil, S. *Cryst. Growth Des.***2010**, 10, 1688.

**20.** Zhao, M.; Zheng, L.; Li, N.; Yu, L. *Mat. Lett.***2008**, 62, 4591.

**21.** Zhang, Y.; Shi, E. –W.; Chen, Z. –Z.; Xiao, B. *Mater. Lett.* **2008** ,62, 1435.

**22.** Liu, J.; Chen, X.; Wang, W.; Huang, Q. *Mater. Lett.* **2009**, 63, 2221.

**23.** Zhu, H. G.; Huang, J. F.; Pan, Z. W.; Dai, S. *Chem. Mater.* **2006,** 18, 4473.

**24.** Zhang, J.; Wang, J.; Zhou, S.; Duan, K.; Feng, B.; Weng, J.; Tang, H.; Wu, P. *J. Mater. Chem.* **2010**, 20, 9798.

**25.** Dong, W. S.; Li, M. Y.; Liu, C. L.; Lin, F. Q.; Liu, Z. T. *J. Colloud Interface Sci.* **2008**, 319, 115.

**26.** Li, L. L.; Zhang, W. M.; Yuan, Q.; Li, Z. X.; Fang, C. J.; Sun, L. D.; Wan, L. J.; Yan, C. H. *Cryst. Growth Des.***2008**, 8, 4165.

**27.** Wang, W. W.; Zhu, Y. J. Inorg. *Chem. Commun.* **2004**, 7, 1003.

**28.** Li, Z. H.; Gessner, A.; Richters, J. P.; Kalden, J.; Voss, T.; Kubel, C.; Taubert, A. *Adv. Mater.* **2008**, 20, 1279.

**29.** Li, Z. H.; Shkilnyy, A.; Taubert, A. *Cryst. Growth Des.* **2008**, 8, 5246.

**30.** Zhong, Z.; Yin, Y.; Gates, B.; Xia, Y. *Adv. Mater.* **2000**, 12, 206.

**31.** Zhao, Q.; Gao, X.; Bai, X.; Wu, C.; Xie, Y. *Eur. J. Inorg. Chem.***2008**, 122.

**32.** Yang, H. X.; Qian, J. F.; Chen, Z. X.; Ai, X. P.; Cao, Y. L. *J. Phys. Chem. C* **2007**, 111, 14067.

**33.** Lee, J. –H. *Sens. Actuators B***2009**, 140, 319.
**34.** Yoo, K.; Choi, H.; Dionysiou, D. D. *Chem. Commun.* **2004**, 2000.
**35.** Zhou, S. H.; Ma, Z.; Beaker, G. A.; Rodinone, R. J.; Zhu, Q.; Luo, H. M.; Wu, Z. L.; Dasi, S. *Langmuir* **2009**, 25, 7229.
**36.** Li, N.; Du, K.; Liu, G.; Xie, Y; Zhou, G.; Zhu, Z.; Li, F.; Cheng, H. M. *J. Mater.Chem. A* **2013**, 1, 1536.